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SIZE EFFECTS ON THE TRANSPORT COEFFICIENT OF LIQUID LITHIUM, SODIUM AND POTASSIUM USING A SOFT SPHERE POTENTIAL

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Abstract

The dependence of the self diffusion coefficient of atoms in liquid Lithium, Sodium and Potassium, interacting through a soft sphere potential, on the number of atoms have been investigated using Molecular Dynamics Simulation at various temperatures. Our calculations predict non-linear relationship between the diffusion coefficient and the number of particles at high densities and medium or low temperatures. The radial distribution function obtained agrees well with experiment.

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1 Introduction

The study of transport properties of liquid alkali metals attracted much interest both theoretically and experimentally [1] – [4]. Although, the dependence of the transport coefficients on temperature has been extensively investigated[4, 5], these studies have always assumed the thermodynamic limit in which the particles in a system are assumed to interact even at large separations. It is well known in simulation that the introduction of periodic boundary conditions should eliminate the overall size effects in a simulation. However, the inclusion of a cut-off radius affects the accuracy of the calculated properties. One then has to add correction terms to the calculated properties. A motivation for this work stems from the above statement: how the use of periodic boundary conditions and the introduction of cut-off radius affect the properties of a liquid system in simulations. The cut-off radius used in our calculations is 1/2L, where L is the size of the simulation box.

In this work the dependence of the number of particles on transport coefficient of liquid lithium, sodium and potassium at various experimental temperatures and densities has been investigated using the method of Molecular Dynamics (MD) simulation.

2 Method of calculation

The formalism of interatomic pair potential in condensed matter has been presented in a number of literatures [6] – [8]. However, for reason of coherence, we present here some of the approaches to a certain extent.
It is possible to write the total potential energy of a classical system consisting of N pairwise interacting atoms enclosed in a volume V as:

$$v(r_{ij}) = \frac{1}{2}\sum_{ij}\phi(r_{ij}) \tag{1}$$

where $\phi(r_{ij})$ is the pair potential between pair of atoms. The summation in eqn.(1) is a double summation over all atoms, the factor of 2 in the denominator is included to avoid over counting in the summation. The above equation also depends only on the nuclear charges and the interaction distance. We have made the above statement, bearing in mind that our assumption is reasonably well justified only at high energies and may not be as good at low energies. Attractive forces become significant if potentials are required at very low energies. There are a number of commonly used attractive potentials in simulation, because of the simplicity and cost effectiveness.

One such attractive potential is the Lennard-Jones potential [9], which is used in this work. This potential was initially used for closed shell elements [10] – [12], however, with good choice

of parametrization, it is equally good for modelling some other types of systems [13] − [16]. Generally, the Lennard-Jones potential is of the form:

$$\phi(r) = 4\epsilon\left[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}\right] \tag{2}$$

The repulsive term is given by the first term, where the second term, which is induced by the dipole-dipole interactions leading to the weak van der Waals forces is the attractive part. In eqn.(2), ϵ and σ respectively represent the well depth of the potential and the atomic diameter. The potential is truncated and shifted, this makes the potential and forces not to vanish at distances above the cut-off radius, that is:

$$\phi(r) = \begin{cases} \phi(r_{ij}) - \phi(r_c) & if \quad r \leq r_c \\ 0 & if \quad r > r_c \end{cases} \tag{3}$$

Molecular dynamics simulation were performed on a system containing 200, 400 and 800 atoms, the simulation box was repeated in space, initial configuration of fcc was assigned to atoms in the system, while velocities of atoms were set to zero. The mass, m of an atom is set to unity for convenience. Interactions beyond distance $r_c = \frac{1}{2}L$ are set to zero. In this case L is the length of the simulation box. The following units were used, distance in unit of σ, energy in unit of ϵ, temperature in unit of $\frac{\epsilon}{K_B}$ and time in unit of $\sigma\sqrt{\frac{m}{\epsilon}}$. The parameters ϵ and σ are taken from literature [17]. The density is given in unit of $\rho\sigma^3$. The initial fcc configurations were melted by allowing the Newton's equation of motion to heat up the system from the zero velocity configurations and scaling the velocities with the square root of the ratio of the temperature and the motion energy. The Verlet algorithm [18] was used in the integration of the equation of motion with a time step of $\Delta t = 0.004$, where the total number of time steps is above 3000. This time step is acceptable as long as the energy and momentum are conserved to the desired accuracy and that the time step should always be much "shorter" than any relaxation time observed or expected in the system.

The internal energy per atom is calculated as the sum of the potential and kinetic terms, this is given as:

$$E_{Tot} = \frac{1}{N}\left\langle \frac{1}{2}\sum_{i}^{N} m_i v_i^2 + V(r_{ij}) \right\rangle \tag{4}$$

Here, $V(r_{ij})$ is as given in eqn.(1). To calculate the pressure, we use:

$$P = \rho^2\left\langle \sum_{i}^{N} m_i v_i^2 + \sum_{i}^{N-1}\sum_{j>i}^{N} r_{ij}\frac{dV(r_{ij})}{dr_{ij}} \right\rangle \tag{5}$$

To check the accuracy of eqns.(4) and (5), we have calculated the total energy and the pressure from the pair distribution function $g(r)$ respectively from:

$$\frac{U}{N} = \frac{1}{2}\rho \int_0^\infty g(r)\phi(r)dr \tag{6}$$

$$= 2\pi\rho \int_0^\infty r^2 g(r)\phi(r)dr \tag{7}$$

and

$$P = \rho T - \frac{1}{6}\rho^2 \int_0^\infty r^2 g(r)\frac{d\phi(r)}{dr}dr \tag{8}$$

$$= \rho T - \frac{2}{3}\pi\rho^2 \int_0^\infty r^3 g(r)\frac{d\phi(r)}{dr}dr \tag{9}$$

Here, $\frac{U}{N}$ is the potential energy per atom.

The pair distribution function has been calculated using:

$$g(r) = \frac{n(r)}{\Delta r \rho} \tag{10}$$

where $n(r)$ is the average number of atoms that can be found between the distance

$$r - \frac{\Delta r}{2} < r < r + \frac{\Delta r}{2} \tag{11}$$

centred around an arbitrary atom. Structural calculations of the $g(r)$ were obtained by collecting configurations during the run at every 5 time steps. We have obtained the $g(r)$ by reading the collected configurations and using the calculated distance between atomic pairs to construct a histogram. Normalization of the histogram was based on the method described in literature [19].

Using the Green-Kubo (GK) relation [20], we calculated the transport coefficients such as the diffusion coefficient D and the viscosity η. The diffusion coefficient can be calculated by starting with the Fick's law of diffusion

$$j = -D\nabla c \tag{12}$$

where j is the flux of diffusing species, c is the concentration and D is known as the proportionality constant called the diffusion coefficient. The time evolution of the concentration profile of eqn.(12) is then given as [20]

$$\nabla . j(r,t) = -\frac{\partial c}{\partial t} \tag{13}$$

By combination, eqns.(12) and (13) become:

$$\frac{\partial^2 c}{\partial t^2} - D\nabla^2 c = 0 \tag{14}$$

The above equation where $c = c(r,t)$ can be solved with the boundary condition such that:

$$c(r,t) = \delta(r) \tag{15}$$

here, $\delta(r)$ is the Dirac delta function. The solution of eqn.(14) is:

$$c(r,t) = \frac{1}{(2\pi Dt)^{\frac{d}{2}}} \exp\left(-\frac{r^2}{2Dt}\right) \tag{16}$$

where d is the dimension of the system. By imposing the condition that:

$$\int c(r,t)dr = 1 \tag{17}$$

Then the second moment of eqn.(16) will be given as:

$$< r^2(t) >= \int c(r,t)r^2 dr \tag{18}$$

The time evolution of $< r^2(t) >$ is then obtained using eqn.(14):

$$\frac{\partial}{\partial t}\int c(r,t)r^2 dr = D\int \nabla^2 c(r,t)r^2 dr \tag{19}$$

leading to:

$$\frac{\partial < r^2(t) >}{\partial t} = 2dD \tag{20}$$

eqn.(19) is the so-called Einstein relation, it connects the mean square displacement with the diffusion coefficient in liquid systems. The form of eqn.(20) that entered into our simulation is actually:

$$< \Delta r(t)^2 >= \frac{1}{N}\sum_{i=1}^{N} \Delta r_i(t)^2 \tag{21}$$

where $< \Delta r(t)^2 >$ is called the mean square displacement. On the other hand, the Green-Kubo relation for the diffusion coefficient is given as [20] :

$$2D = \lim_{t\to\infty} 2\int_0^t < v(t-t').v(0) > dt' \tag{22}$$

therefore,

$$D = \int_0^\infty < v(\tau).v(0) > d\tau \tag{23}$$

This is the Green-Kubo equation for the diffusion coefficient, where $\tau = t - t'$ and $< v(\tau).v(0) >$ is a measure of correlation between the velocity of an atom at times $t - t'$ and $t = 0$. It is also known as the velocity autocorrelation function.

Similarly, for the viscosity, the Green-Kubo relation is given as [11,22]:

$$\eta = \frac{1}{VK_BT}\int_0^\infty \Big\langle \sigma_{xy}(t).\sigma_{xy}(0) \Big\rangle dt \tag{24}$$

where σ_{xy} is defined as:

$$\sigma_{xy} = \sum_{i=1}^{N} m_i v_{ix} v_{iy} + \frac{1}{2}\sum_{i=1}^{N-1}\sum_{j>i}^{N} r_{ij} f(r_{ij}) \tag{25}$$

We waited for the total number of time steps of over 1000 for the system to melt from initial configuration and another 2000 time steps before samples were taken for analysis. The time step Δt used in each simulation is such that it is "shorter" than the relaxation time of the system as mentioned earlier on.

3 Results and discussion

Liquid alkali metals have undergone several theoretical and experimental studies [4-5, 22-27] of structural and transport properties, using methods of molecular dynamics. We performed molecular dynamic simulations for liquid alkali metals at thermodynamic states for which experimental data are available [21]. The thermodynamic states are given in Tables 1-3. These tables also contain calculated single-particle coefficient, the diffusion coefficient, D. Reduced units are used to check the universality of the behaviour of D at each chosen thermodynamic state of all the alkali metals studied. These units are already given in Section 2 above. In Fig.1, the pair distribution functions $g(r)$ obtained in our simulations are presented and are compared with the experimental data of ref. [21]. There is agreement between the two results except for a slight difference in the height of the first peak. This agreement justifies the correctness of our choice of potential model.

In Tables 1-3, at each temperature, simulation is performed using 200 atoms in the central box, the simulation is then repeated for 400 atoms and 800 atoms. Experimental density is used to determine the volume of the simulation box in each case and based on the number of atoms. The values of the diffusion coefficient obtained without adding correction term are shown in the fourth column of the tables. In all the cases studied, we obtained a non-linear curve of the dependence of D on N. Given that at each thermodynamic state, the density and temperature are fixed while the number of atoms varies, there is a consequence change in volume leading also to local change in pressure around an atom.

When the number of atoms in the cut-off range is increased, we expect a corresponding increase in pressure in the central box, but the total pressure remains the same, since temperature is not changing. Therefore, only the local pressure on an atom changes and this permits such atom to either increase or decrease its motion thereby affecting the flux of atoms. When 200 atoms are packed in the simulation box, the local pressure on an atom is high due to the fact that the atoms are closely packed within the length L of the box. The diffusion coefficient is low in this case since the flux of diffusing atoms will be small. With 400 atoms however, the case is such that atoms have a larger volume to occupy, in fact, the volume occupied will be twice as in the case of 200 atoms, leading to a decrease in local pressure on an atom with the consequence higher flux of diffusing atoms leading to higher diffusion coefficient.

The slight decrease in D when N is increased to 800 atoms could be as a result of an increase in the mean free path when volume increases. Atoms are less frequently bumping into one another with lower collective motion and giving rise to decrease in flux of diffusing atoms. The pair distribution function $g(r)$ obtained from the simulations are shown in Fig.1, which also shows

the corresponding experimental data [21]. For convenience, we have only shown results at high temperature in each case.

The calculated results stand remarkably well with experiments except for the slight difference in height of the first peak which we attribute to the values of ϵ used in our simulation. Generally, the figure also shows that the effect of the number of atoms in the simulation on the structure is neglegible, this is true since at large distances the correlation between pair of atoms disappears. As already discussed above pertaining to Tables 1-3, Fig.2 shows the non-linear relationship between D and N.

4 Conclusion

In this work, we have presented a study of the dependence of the diffusion coefficient in liquid alkali metals on the number of particles. In each of the cases studied, we have used 200, 400 or 800 particles with periodic boundary conditions. The introduction of a cut-off radius leads to a non linear dependence of the diffusion coefficient on the number of atoms in the systems studied.

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Table 1: Dependence of Diffusion Coefficient on number of atoms from MD simulation of liquid Li

System	T^*	ρ^*	D	N
Li	0.190	0.714	0.03092	200
Li	0.190	0.714	0.05634	400
Li	0.190	0.714	0.04495	800
Li	0.194	0.725	0.02946	200
Li	0.194	0.725	0.06641	400
Li	0.194	0.725	0.05237	800

Table 2: Dependence of Diffusion Coefficient on number of atoms from MD simulation of liquid Na

System	T^*	ρ^*	D	N
Na	0.264	1.016	0.07716	200
Na	0.264	1.016	0.27334	400
Na	0.264	1.016	0.24661	800
Na	0.295	0.995	0.07296	200
Na	0.295	0.995	0.25750	400
Na	0.295	0.995	0.22503	800
Na	0.358	0.961	0.06967	200
Na	0.358	0.961	0.23550	400
Na	0.358	0.961	0.21062	800
Na	0.452	0.932	0.06813	200
Na	0.452	0.932	0.20817	400
Na	0.452	0.932	0.18759	800
Na	0.576	0.906	0.07177	200
Na	0.576	0.906	0.20995	400
Na	0.576	0.906	0.17540	800

Table 3: Dependence of Diffusion Coefficient on number of atoms from MD simulation of liquid K

System	T^*	ρ^*	D	N
K	0.258	0.991	0.07552	200
K	0.258	0.991	0.25249	400
K	0.258	0.991	0.21805	800
K	0.356	0.968	0.06998	200
K	0.356	0.968	0.24291	400
K	0.356	0.968	0.20754	800
K	0.469	0.928	0.07005	200
K	0.469	0.928	0.21414	400
K	0.469	0.928	0.19284	800
K	0.544	0.897	0.06668	200
K	0.544	0.897	0.19244	400
K	0.544	0.897	0.17581	800

Figure 1: At long distance, we show the effect of the cut-off radius in liquid alkali metals.

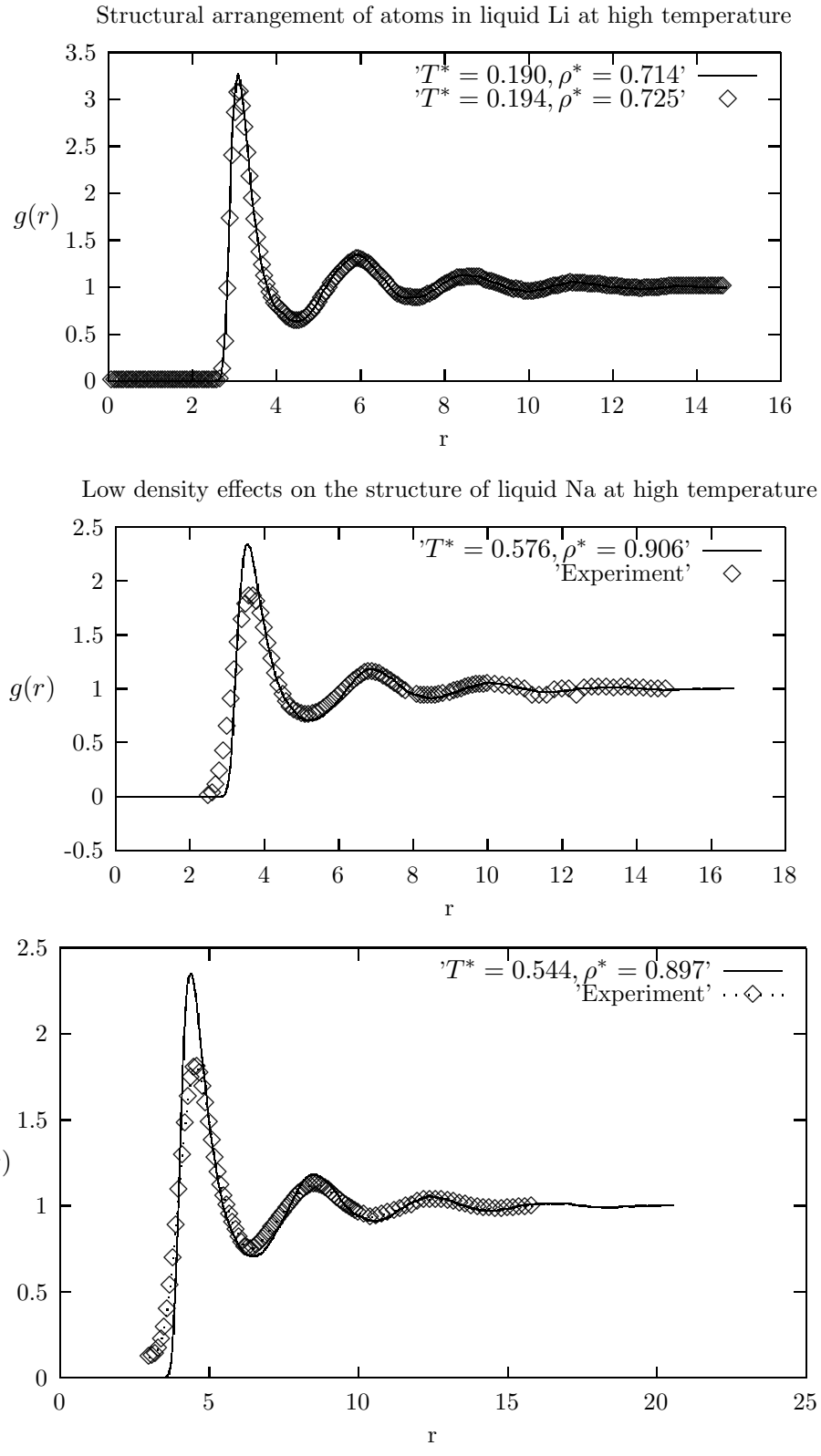

Figure 2: Variation in diffusion coefficient in liquid alkali metals with number of atoms. The thermodynamic states are as given in the key.